

# Mixed sodium and calcium ions affects permeability and ion exchange transport behaviour in saline-sodic soil

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## 1. Abstract

Sodium (Na) and calcium (Ca) ions are the most common ions on the exchange complex, particularly in the arid and semi-arid saline-sodic soils. We examined the effects of the composition of mixed Ca and Na ions on the soil permeability and Na-Ca exchange behaviour for an agricultural sodic soil by carrying out ion exchange transport experiments in saturated columns. Generally the permeability was found to decrease with increasing sodium adsorption ratio (SAR) and decreasing electrolyte concentration. This reduction was attributed to partial blocking of pores by dispersed clay particles, as evidenced by the appearance of suspended clay particles in the effluent during leaching. However, this mechanistic behaviour or “critical threshold and turbidity concentration” occurred at SAR 15. The Na-Ca breakthrough curves at SAR 15 showed an initial increase in the effluent Na following commencement input of the 10mmol/L and subsequently decreased rapidly with decreased input solution to 2.5mmol/L. The effluent Ca concentration decreased progressively with the decreasing input solution. In most cases measured pHs of the solution were found to remain essentially constant during leaching while the electrical conductivity decreased with decreasing electrolyte concentration.

**Keywords:** sodium adsorption ratio, permeability, calcium and sodium ions, breakthrough curves

## 2. Introduction

Saline and sodic conditions are frequently observed in semi-arid regions with the deterioration in permeability alleviated by maintaining the electrolyte concentration of percolating water above a critical threshold level (Levy *et al.* 2005). Problems related to the use of sodic/saline waters are global (Szabolcs 1992) especially in arid and semi-arid soils where the sodium (Na) and calcium (Ca) ions are the most common ions on the exchange complex (Miller and Donhue 1995). The behaviour of the ions on the exchange complex affects mechanism of ionic transport (Ersoz *et al.* 2001) with the cation exchange reactions being affected by exchanger species between solution and adsorbed phases (Evangelou and Lumbanraja 2002). The cation exchange behaviour for the Na-Ca exchange system (Gapon 1933) is described by;

$$\frac{Na_x}{Ca_x} = K_G * \frac{[Na]}{[Ca]^{0.5}} \quad \text{or} \quad ESR = K_G * (SAR) \quad \text{with} \quad SAR = \frac{[Na]}{\sqrt{[Ca]}} \quad (1) \text{ and}$$

$$CEC = E_{xNa} + E_{xCa} \quad (2)$$

where  $CEC$  is the cation exchange capacity and  $E_{xNa}$  and  $E_{xCa}$  is the activity of exchange phase of Na and Ca respectively.  $Na_x$  and  $Ca_x$  are fractions of the exchange complex occupied by those ions,  $K_G$  is the Gapon constant and the square brackets indicate concentrations (in mmol/L) of the ions in solution, ESR is the exchangeable sodium ratio and SAR is the sodium adsorption ratio.

Excessive sodium ions on the exchange complex enhance swelling and dispersion which may have profound effects on soil structural stability of the pore matrix and decrease of permeability (Keren and Ben-Hur 2003) with decrease in electrolyte concentration particularly with increased SAR. For example an increase in SAR can cause soil structural deterioration through clay swelling and dispersion and by slaking of silt-sized micro-aggregates (Abu-Sharar *et al.* 1987) thus blocking the water conducting pores. Further, using a monovalent NaCl electrolyte solution, Dikinya *et al.* (2006) attributed the decrease of permeability to mobilization and re-deposition of fine particles. Little, if any, research work dealing with the combined effects of salinity on the dynamics of permeability and ionic transport have been carried out.

The objectives of study are two-fold; (a) to examine the effects of the sodium adsorption ratio at decreasing electrolyte concentration on permeability and (b) to assess the Na-Ca exchange reactions and dynamics of the electrolyte breakthroughs in saturated soil columns.

### 3. Materials and Methods

#### 3.1 Soil materials

An agricultural soil sandy loam sample collected from top 20 cm of the soil for analysis and transport measurements. The soil often shows some build up of salts, especially sodium, in the subsoil, and has a potential for structural breakdown. The basic physico-chemical properties of the soil measured using standard methods (Klute, 1986) are presented in Table 1.

**Table 1 Selected physico-chemical characteristics of soil samples measured**

Property	Units	Value
Sand fraction	%	83.3
Silt fraction	%	6.6
Clay fraction	%	10.1
Bulk Density	g/cm <sup>3</sup>	1.61
Electrical conductivity	μS/cm	42
pH( water)	-	6.1
Cation exchange capacity (CEC)	cmol/kg	3.4
Exchangeable sodium percentage (ESP)	%	2.5

#### 3.2 Binary exchange reactions

Exchange reactions of Na-Ca were carried out using a batch technique for samples described in Table 1. Ten grams of each sample in triplicate were saturated with the binary pair of Na-Ca using 30 mL solution of the following cation (Na/Ca) ratios: r; 0.9, 0.7, 0.4, 0.2 and 0.1 and each added into separate 50 mL centrifuge tubes. The 30 mL Na/Ca mixtures were initially saturated with 0.5 M solution for equilibration with exchanger sites. The 0.5M saturated samples were shaken for 24 hours (to dislodge aggregates), then centrifuged with supernatant discarded. This procedure was repeated twice, followed by 0.005 M solutions by repeating the above procedure six (6) times to ensure equilibration. The 30 mL ammonia acetate (1M NH<sub>4</sub>OAc), adjusted to a soil pH 6 (using acetic acid and ammonium hydroxide solution), was added to the supernatant for the cationic extraction. The supernatants were then analysed for cationic exchange capacities using Atomic Adsorption Spectrometer (AAS).

#### 3.3 Permeability and Breakthrough curves

Soil samples (< 2 mm) were initially mixed with 0.9-1 mm acid-washed sand (50% sand and 50% soil) to provide a rigid skeletal structure and to enhance water flow. The mixture was uniformly wet packed at density of 1.69 g/cm<sup>3</sup> in a column (400mm long; 25mm diameter), with pressure transducers connected to holes bored at depths ;D<sub>1</sub>(50mm), D<sub>2</sub> (150mm) and D<sub>3</sub> (250 mm) from the inlet for pressure head measurements. The columns were then saturated with the desired solutions of different SARs: 5, 15 and 30 and with varying electrolyte concentrations; 1, 10 and 100 mmol/L and left over night for a complete saturation. A peristaltic pump was used to pump the feed solutions at constant flow rate of 1 cm<sup>3</sup>/min while an Agilent data logger system (Agilent Technologies, 2003) was used for online pressure head measurements data capture. For the cationic Na/Ca breakthrough curves, the columns were initially saturated by passing 10 pore volumes of 10mmol/L CaCl<sub>2</sub> until equilibrium. After this pre-conditioning the input solution was progressively changed through 10, and 2.5mmol/L at SAR 15. The solutions were then leached with about 18 pore volumes and with the effluents collected in fraction collectors used measurements of pH, EC and Na/Ca concentrations analysis by Atomic Absorption Spectrometer (AAS) to obtain breakthrough curves.

## 4. Results and discussions

### 4.1. Binary exchange reactions

The experimental data on Ca-Na exchange on solution and exchange phases are presented in Table 2. Changes in total exchange capacity ( $\Sigma\text{Exi}$ ) demonstrated a non-exchanger preference for  $\text{Ca}^{2+}$  than  $\text{Na}^{+}$  ions. This minor variation in  $\Sigma\text{Exi}$  was consistent with smaller variation in exchanger phase composition suggesting nearly constant surface uniformity throughout the entire exchange isotherm. Similarly there were minor variations of solution pH (6.1 - 6.6) across the entire isotherms of the Na-Ca binary systems (Table 2).

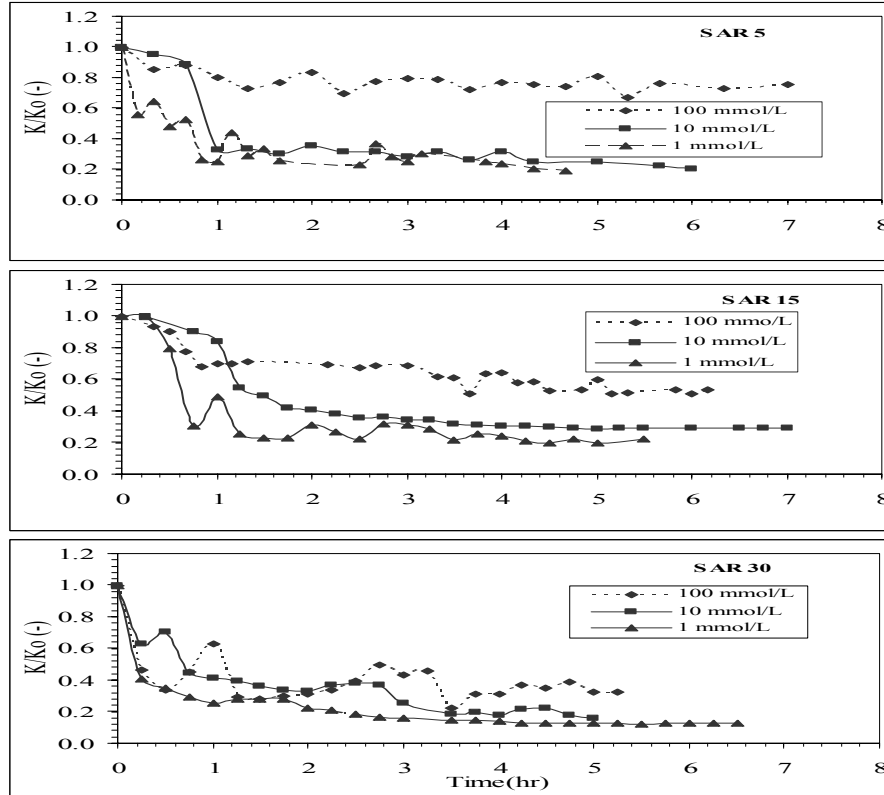
**Table 2 Sodium-Calcium exchange on soils for different concentrations ratios r**

r (Na/Ca)	pH	ExNa (mmol/kg)	ExCa (mmol/kg)	$\Sigma\text{Exi}$ (mmol/kg)
0.9	6.1	1.10	11.50	12.60
0.7	6.6	0.64	11.10	11.74
0.4	6.3	0.46	11.14	11.86
0.2	6.6	0.20	12.50	12.70
0.1	6.6	0.18	12.20	12.38

Exi- denotes concentration of adsorbed cations and  $\Sigma\text{Exi}$ - total adsorbed cations

### 4.2 Effects of sodium adsorption ratio on permeability

The relative permeability ( $K/K_0$ ), [where  $K_0$  and  $K$  is the initial and actual measured permeability, respectively], measured as a function of electrolyte concentration, following leaching of the soil columns with solutions of SAR 5, 15, and 30 are shown in Figure 1. Generally,  $K/K_0$  decreased with time, with increasing SAR and with decreasing electrolyte concentrations.



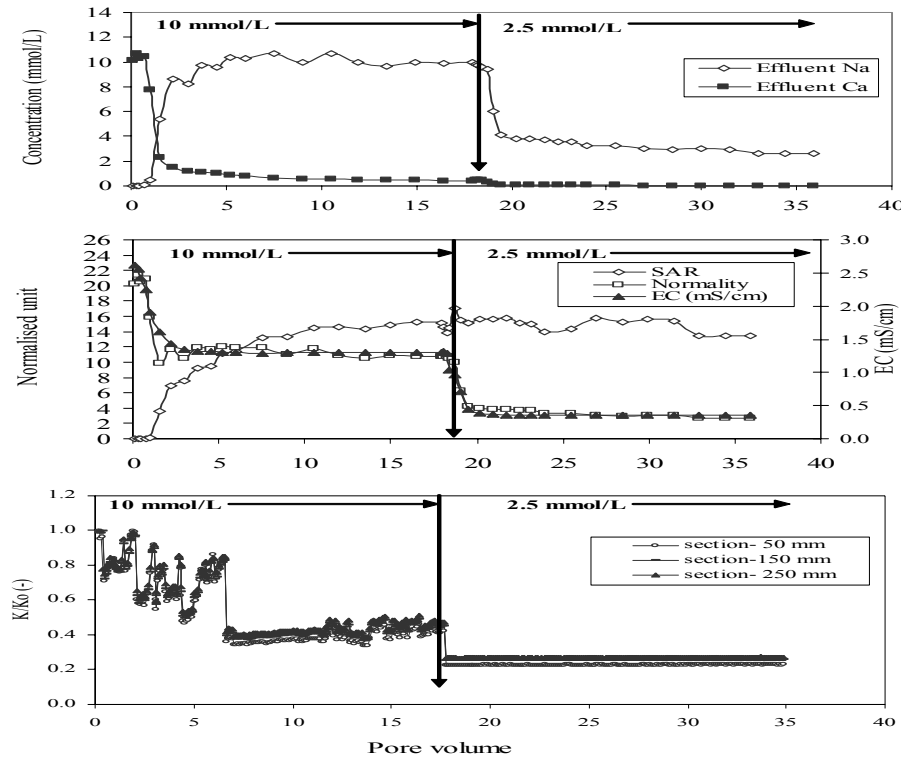
**Figure 1 Permeability ( $K/K_0$ ) as function of electrolyte concentration for various sodium adsorption ratio (SAR) and time (hr) at column depth  $D_1$  (50 mm from inlet)**

It was clear that  $K/K_0$  was maintained at SAR 5 for 100 mmol/L but decreased rapidly at lowest concentrations for all SARs. This is because the dilution of high-sodic soil irrigation water can cause swelling, aggregate slaking and particle clay dispersion (Abu-Sharar et al., 1987) and the reductions in  $K/K_0$  here were likely

to be caused by partial blocking of pores by dispersed clay particles, as evidenced by the appearance of suspended clay particles in the effluent during leaching. However the initial and the final pH remained constant during leaching whereas the EC decreased with decreasing electrolyte concentration suggesting an influence of EC on salinisation and particle pore clogging to reduce  $K/K_o$ .

#### 4.3 Breakthrough curves and permeability at critical concentrations

Figure 2 shows the permeability and breakthrough curves following column leaching with SAR 15 solution at 10 mmol/L followed by 2.5 mmol/L. The SAR 15 was observed as critical threshold and turbidity concentration as evidenced by structural collapse and dispersed clay leaving the system during leaching. Equilibrium was maintained after 18 pore volumes, with the input equal the output Na/Ca concentrations. An initial increase in the Na effluent concentration following commencement of the input of the 10mmol/L at SAR 15 solution occur rapidly, and is followed by subsequent rapid decreases with decreasing electrolyte concentration of the input solution to 2.5mmol/L. The Ca concentrations in the effluent decreased progressively with decreasing input concentrations. The rapid decrease in  $K/K_o$ , at this critical concentration, presumably reflects a more open pore structure associated with the presence of micro-aggregates. The electrical conductivity closely follows the decrease with normality of the solutions.



**Figure 2 Breakthrough curve (Na-Ca exchange reactions) following leaching with SAR 15 (at Threshold concentration 10 mmol/l, and Turbidity concentration-2.5 mmol/L respectively): Effects on normality, sodium adsorption ratio (SAR) on permeability**

A most surprising feature of the results is the relative uniformity of the response at the different measuring points along the column despite the clear indication of a gradual breakthrough of the SAR front moving through the columns during the change from the 10 to 2.5 mmol/L at SAR 15. This change is initially accompanied by rather erratic  $K/K_o$  behaviour before near uniformity occurs. At the threshold concentration one would expect slaking to occur with perhaps some dispersion. The subsequent reduction in input concentration to 2.5mmol/L (the turbidity concentration) occurs rapidly in the effluent producing uniformly lower  $K/K_o$  along the columns.

#### 5. Summary and conclusions

Permeability ( $K/K_o$ ) has been shown to decrease with time, with increasing SAR and with decreasing electrolyte concentration with more rapid decrease at the lowest concentration (1 mmol/L). Significant differences in

K/Ko were observed in the passage of fronts of decreasing electrolyte concentrations through the soil columns reflecting structural alterations (slaking) within the porous structure at any given point in the column. The effluent Ca concentration decreased progressively with the decreasing input solution while measured pHs of the solution remain constant during leaching and EC decreased with decreasing electrolyte concentration.

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